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Short communication

Use of nitrogen to remove solvent from through oven transfer adsorption desorption interface during analysis of polycyclic aromatic hydrocarbons by large volume injection in gas chromatography

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ABSTRACT

The through oven transfer adsorption desorption (TOTAD) interface allows large volume injection (LVI) in gas chromatography and the on-line coupling of liquid chromatography and gas chromatography (LC–GC), enabling the LC step to be carried out in normal as well as in reversed phase. However, large amounts of helium, which is both expensive and scarce, are necessary for solvent elimination. We describe how slight modification of the interface and the operating mode allows nitrogen to be used during the solvent elimination steps. In order to evaluate the performance of the new system, volumes ranging from 20 to 100 μL of methanolic solutions of four polycyclic aromatic hydrocarbons (PAHs) were sampled. No significant differences were found in the repeatability and sensitivity of the analyses of standard PAH solutions when using nitrogen or helium. The performance using the proposed modification was similar and equally satisfactory when using nitrogen or helium for solvent elimination in the TOTAD interface. In conclusion, the use of nitrogen will make analyses less expensive.

1. Introduction

Large volume injection (LVI) in gas chromatography (GC) increases sensitivity and/or reduces the need for extract concentration, making it particularly appropriate when compounds have to be determined at very low concentrations. LVI techniques can serve as an interface for the on-line coupling of liquid chromatography–gas chromatography (LC–GC) [1,2] since the problem involved in both techniques is similar: the introduction in GC of a large volume of sample, extract or eluent coming from LC. Multidimensional chromatographic techniques, such as LC–GC, are excellent tools to analyze complex samples [3]. LC–GC is a very powerful technique, and offers the possibility of injecting large volumes of dirty samples. Besides this technique presents important advantages since the LC step can replace sample preparation steps [3], in this way the analysis is faster and more sensitive. The LC–GC should be performed since robust interfaces, preferably automated. Several reviews on LC–GC coupling have described different interfaces [4–7]. However, only a few of these interfaces allow the direct introduction of water in GC. The use of polar solvents, especially water, presents a number of difficulties. Water in GC analysis [2] is an aggressive solvent that spoils the performance of the GC column. Venting large amounts of water is a time-consuming process and requires high temperatures due to the high boiling point and the larger volume of vapour formed than in the case of a non-polar solvent.

The versatile interface named through oven transfer adsorption desorption (TOTAD), described by Perez et al. [8], allows the large volume injection of both polar and non-polar solvents. This interface, which is totally automated, represents a substantial modification of a PTV. The changes introduced affect the pneumatics, sample introduction, solvent elimination and operation mode. The gas flow can reach the interface through two inlets: the usual carrier gas inlet of a PTV injector (inlet A) (Fig. 1) and the usual split exit (inlet B), which is used as inlet in the TOTAD interface. Initially, the gas enters through both inlets. A liner packed with packing material is inside the body of the interface. When the sample is transferred to the liner, the gas flow entering through (B) pushes the solvent to waste and the gas flow entering through (A) prevents condensation of the vented solvent (see Fig. 1). The analytes are retained on the sorbent. Once the transfer step is completed the helium flow is kept constant for an additional time to ensure that all the

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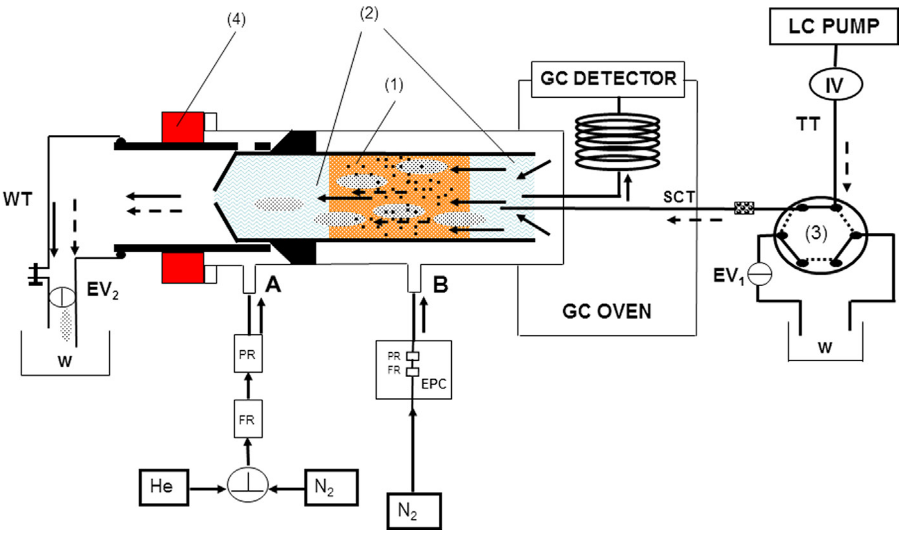

Fig. 1. Scheme of the TOTAD interface during injection step. *Symbols*: (1) packing material; (2) glass wool; (3) six-port valve; (4) heated cover; (SCT) silica capillary tubing, 0.32 mm i.d.; (WT) waste tubing; (TT) transfer tubing; (IV) LC manual injection valve; (⊖) electro valve; (⟶) gas flow; (- - -►) liquid flow; (PR) pressure regulator; (▦) filter; (⊣) needle valve; (FR) flow regulator, (⊕) 3 way valve, (w) waste, (EPC) electronic pressure control

remaining solvent is eliminated and then the gas flow through B is shut off and gas enters only through A to be used as carrier gas during the analysis step.

This interface has the great advantage that it allows operation with both non-polar and polar solvents, even water, but it has the drawback of needing a high amount of helium to remove the solvent.

As is well known, helium is not an unlimited resource. In 2013, the Responsible Helium Administration and Stewardship Act was approved by the U.S. House and Senate [9]. The legislation would restrict the distribution of helium from the U.S. national reserve, which makes up about 30 percent of the world's helium. While chromatographers can use hydrogen or nitrogen as alternatives to helium, the most important argument against the use of hydrogen concerns safety. And in the case of nitrogen, although it is commonly used as carrier gas in GC, many authors do not recommend nitrogen for this purpose. However, using nitrogen instead of helium in the TOTAD interface during transfer and the remaining solvent elimination steps should not, in principle affect, column efficiency, peak resolution or the speed of analysis, as its role is only to push the solvent to waste. By doing this, helium consumption could be reduced, making the method cheaper and more environmental friendly, while maintaining the performance of the chromatographic system. The goal of the present work was to substantially reduce the consumption of helium per analysis, to this aim a modification of the TOTAD interface that allows the use of nitrogen to eliminate the solvent is presented. The performance of the new system has been tested by sampling large volumes of a standard solution of polycyclic aromatic hydrocarbons (PAHs) in a polar solvent.

2. Experimental

2.1. Materials

Anthracene (Ant) and Fluorene (Fl) standards were obtained from Fluka (Buchs, Switzerland). Benzo(e)pyrene (BeP) standard was obtained from Dr. Ehrenstofer Gmbh (Augsburg, Germany), and Indeno(1,2,3-cd)pyrene (IdP) standard was obtained AccuStandard (New Haven, CT). A standard mixture solution of 100 mg/L of PAHs was prepared in methanol and stored at 4 °C. The working solutions were obtained by diluting the standard mixture in methanol at concentrations ranging from 0.5 to 10 mg/L. The methanol used as solvent and as eluent was HPLC grade from pestican (LabScan, Dublin, Ireland). Tenax TA, 80–100 mesh (Chrompack, Middelburg, Netherlands) was used as packing material in the glass liner of the TOTAD interface. The glass liner was packed with a 1 cm length of Tenax TA between two plugs of glass wool to keep it in place and then conditioned under a helium stream by heating from 50 °C to 350 °C at 50 °C/10 min, and holding for 60 min.

2.2. Instrumentation

A Konik 4000B gas chromatograph, equipped with a TOTAD interface was used. The TOTAD interface (U.S. patent 6,402,947 B1, exclusive rights assigned to KONIK-Tech, Sant Cugat Del Vallés, Barcelona, Spain) was used to inject a large volume of the standard solutions into the GC. For very large volume sampling a manual injection valve (model 7125 Rheodyne, CA) with different volume loops (20, 40, 60, 80, and 100 μL) was used. A ternary LC pump (Konik model 560) was used to propel the standard solutions into the TOTAD interface. Detection was carried out using a Flame Ionization Detector (FID). Data acquisition and processing were performed with KoniKrom Plus (Konik, Sant Cugat Del Vallés, Barcelona, Spain) software.

2.3. TOTAD operation mode

Fig. 1 shows a scheme of the TOTAD interface during the injection step. The operation mode of the TOTAD interface has been extensively described elsewhere [10–13].

The TOTAD interface and GC oven temperature were stabilized at 80 and 60 °C, respectively. Different volumes of standard solutions were injected using the LC manual injection valve. The standard solutions reached the liner at 0.1 mL/min propelled by the LC pump. In the stabilization, transfer, and remaining solvent elimination steps, nitrogen or helium were entered through both inlets. An electronic 3-way valve, which can be automatically switched, was used to select the nitrogen or helium entering through A, keeping the flow at 500 mL/min. In these steps, the gas flowing through A prevents solvent condensation in the zone of the interface surrounding the WT tube. The gas flow through the oven side (inlet B) reaches the body of the interface to vent the solvent. For this inlet, helium and nitrogen were used in order to compare their